Bulk and Interface Balance Equations for Organic Solar Cell Simulation

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Summary. In this communication, we present a computational model for heterojunction Organic Solar Cells (OSCs) consisting of a system of semilinear PDEs and ODEs. The mathematical model is discussed, focusing on the transmission conditions at material interfaces, together with the numerical method used for its solution. Steady-state and transient simulations are performed on realistic devices with various interface morphologies.

1 Introduction and Motivation

In the design of efficient OSCs the impact of material interface morphology on performance is currently considered to be of paramount importance. For this reason, material scientists are putting much of their research effort into techniques for controlling interfaces down to the nanoscale, for example by studying materials that have the ability to self-assemble into ordered nanostructures during the deposition process. For the same reason, computational models that allow to estimate device performance carefully accounting for the material interface geometry and the phenomena occurring on it are in high demand. Previous approaches in this direction can be found in [1] (for biplanar devices) and [7]. In this communication we present our work aimed at extending the model of [1] to treat arbitrary multidimensional morphologies.

2 Mathematical Model

Let Ω be an open subset of $\mathbb{R}^d$, $d = 1,2,3$, representing the geometrical model of an OSC and $\boldsymbol{\nu}$ be the unit outward normal vector over the boundary $\partial\Omega$. The device structure is divided into two open disjoint subregions, Ω_n (acceptor) and Ω_p (donor), separated by a regular surface Γ on which $\boldsymbol{\nu}_\Gamma$ is the unit normal vector oriented from Ω_p into Ω_n. The cell electrodes, cathode and anode, are denoted as Γ_C and Γ_A, respectively (see Fig. 1 for the 2D case). Let e, n and p denote the volumetric densities of excitons, electrons and holes in the cell, respectively, P be the areal density of polaron pairs and φ be the electric potential. For any function $f : \Omega \to \mathbb{R}$, let $[\![f]\!] := f_n - f_p$, f_n and f_p being the traces of f on Γ from Ω_n and Ω_p, respectively. Excitation phenomena occurring in the bulk are described by the parabolic problem:

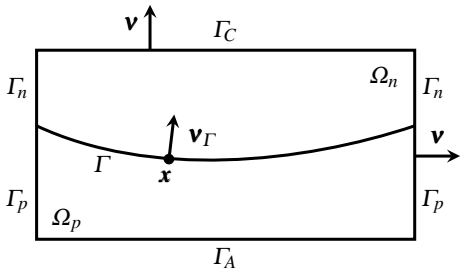

Fig. 1. OSC cell geometry.

$$\begin{cases} \dfrac{\partial e}{\partial t} - \nabla\cdot(D_e\nabla e) = Q - \dfrac{e}{\tau_e} & \text{in } \Omega\setminus\Gamma, \\ [\![e]\!] = 0, & \text{on } \Gamma, \\ [\![-\boldsymbol{\nu}_\Gamma\cdot D_e\nabla e]\!] = \eta k_{\rm rec}P - \dfrac{2H}{\tau_{\rm diss}}e & \text{on } \Gamma, \\ e = 0 & \text{on } \Gamma_C\cup\Gamma_A, \\ e(\boldsymbol{x},0) = 0, & \forall \boldsymbol{x}\in\Omega. \end{cases} \tag{1a}$$

Dissociation/recombination of excitons, electrons and holes into polaron pairs at the material interface is described by the ODE:

$$\begin{cases} \dfrac{\partial P}{\partial t} = \dfrac{2H}{\tau_{\rm diss}}e + 2H\gamma np - (k_{\rm diss}+k_{\rm rec})P & \text{on } \Gamma, \\ P(\boldsymbol{x},0) = 0, & \forall \boldsymbol{x}\in\Gamma. \end{cases} \tag{1b}$$

Transport of photogenerated electrons in the acceptor domain Ω_n is described by the parabolic problem:

$$\begin{cases} \dfrac{\partial n}{\partial t} + \nabla\cdot\mathbf{J}_n = 0 & \text{in } \Omega_n, \\ \mathbf{J}_n = -D_n\nabla n + \mu_n n\nabla\varphi & \text{in } \Omega_n, \\ -\boldsymbol{\nu}_\Gamma\cdot\mathbf{J}_n = -k_{\rm diss}P + 2H\gamma np & \text{on } \Gamma, \\ -\kappa_n\boldsymbol{\nu}\cdot\mathbf{J}_n + \alpha_n n = \beta_n & \text{on } \Gamma_C, \\ n(\boldsymbol{x},0) = 0, & \forall \boldsymbol{x}\in\Omega. \end{cases} \tag{1c}$$

A parabolic problem completely similar to (1c) describes hole transport in the donor domain Ω_p. The dependence of the electric potential and field on the space charge density in the cell is described by the Poisson equation:

$$\begin{cases} \nabla\cdot(-\varepsilon\nabla\varphi) = -qn & \text{in } \Omega_n, \\ \nabla\cdot(-\varepsilon\nabla\varphi) = +qp & \text{in } \Omega_p, \\ [\![\varphi]\!] = [\![-\boldsymbol{\nu}_\Gamma\cdot\varepsilon\nabla\varphi]\!] = 0 & \text{on } \Gamma, \\ \varphi = 0 & \text{on } \Gamma_C, \\ \varphi = V_{\text{appl}} + V_{\text{bi}} & \text{on } \Gamma_A. \end{cases} \quad (1d)$$

A list of the model parameters with their corresponding physical meaning is reported in Table 1. The PDE/ODE model (1) has been introduced in [2] and represents a multi-dimensional generalization of the 1D formulation proposed in [1]. System (1) is completed by periodic boundary conditions on $\Gamma_n \cup \Gamma_p$. We notice that the dissociation and recombination processes occurring at the donor-acceptor interface Γ are dealt with by the nonlinear transmission conditions $(1a)_3$ and $(1c)_2$, whose dependence on the local electric field magnitude and orientation is contained in the polaron dissociation rate constant k_{diss} [2].

Table 1. Model parameters.

Symbol	Parameter
μ_i, D_i	Mobility and diffusivity of species i, $i = e,n,p$
Q	Exciton generation rate
τ_e, τ_{diss}	Exciton decay and dissociation times
k_{rec}, k_{diss}	Polaron recombination and dissociation rates
γ	Electron-hole recombination rate constant
η	Singlet exciton fraction
H	Active layer thickness

3 Algorithms and Simulation Results

System linearization (by a quasi-Newton method) and approximation are carried out by adapting the approach used in [3]. Time advancing is treated using Rothe's method and adaptive BDF formulas, while the exponentially fitted Galerkin finite element method studied in [5] is used for spatial discretization. The interface conditions at the donor-acceptor interface are taken care of by means of the substructuring techniques described in [6].

Model (1) is here validated in both stationary and transient regimes. In a first set of simulations, we study the finger-shaped heterostructure considered in [7]. Fig. 2 shows the output current-voltage characteristics predicted by our model, which is in excellent agreement with that computed in [7]. In a second set of simulations, we test the ability of the model to describe the behaviour of a cell characterized by a complex interface morphology. Fig. 3 shows the free carrier densities computed for a "curly-shaped" geometry at short circuit working conditions. In a third set of simulations, we test the model in the time-dependent case. Fig. 4 shows the cell current response under two different biasing conditions for a planar device geometry similar to that studied in [1]. Ongoing activity is devoted to the investigation of the working principles of the light-harvesting device described in [4].

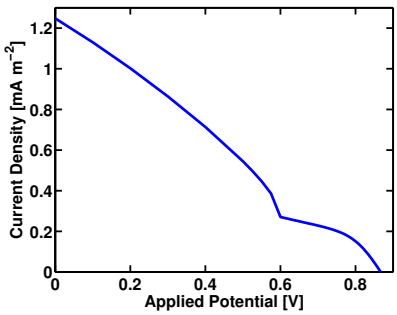

Fig. 2. Current-voltage characteristics for the finger-shaped heterostructure investigated in [7].

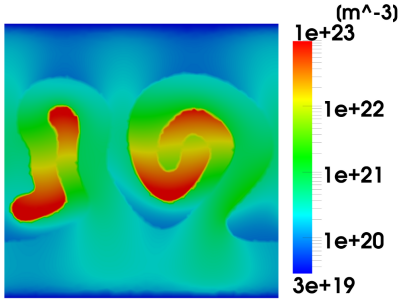

Fig. 3. Free carrier densities for a device with complex morphology.

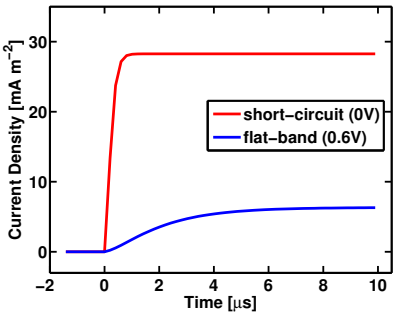

Fig. 4. Contact current density transient at two different voltage regimes.

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